

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
22 November 2001 (22.11.2001)

PCT

(10) International Publication Number  
**WO 01/87464 A1**

(51) International Patent Classification<sup>7</sup>: **B01D 53/50**,  
B01J 10/00, 19/00, C01B 17/80, 17/82, 21/38

**GOLDEN, Claire** [US/US]; 62 Oak Hill Drive, Loudon,  
NH 03301 (US).

(21) International Application Number: PCT/US01/15483

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ,  
DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR,  
HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR,  
LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ,  
NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM,  
TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(22) International Filing Date: 14 May 2001 (14.05.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/204,079 12 May 2000 (12.05.2000) US

(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian  
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European  
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,  
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,  
CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant (*for all designated States except US*): **POWERSPAN CORP.** [US/US]; P.O. Box 219 / 54 Old Bay  
Road, New Durham, NH 03855 (US).

Published:

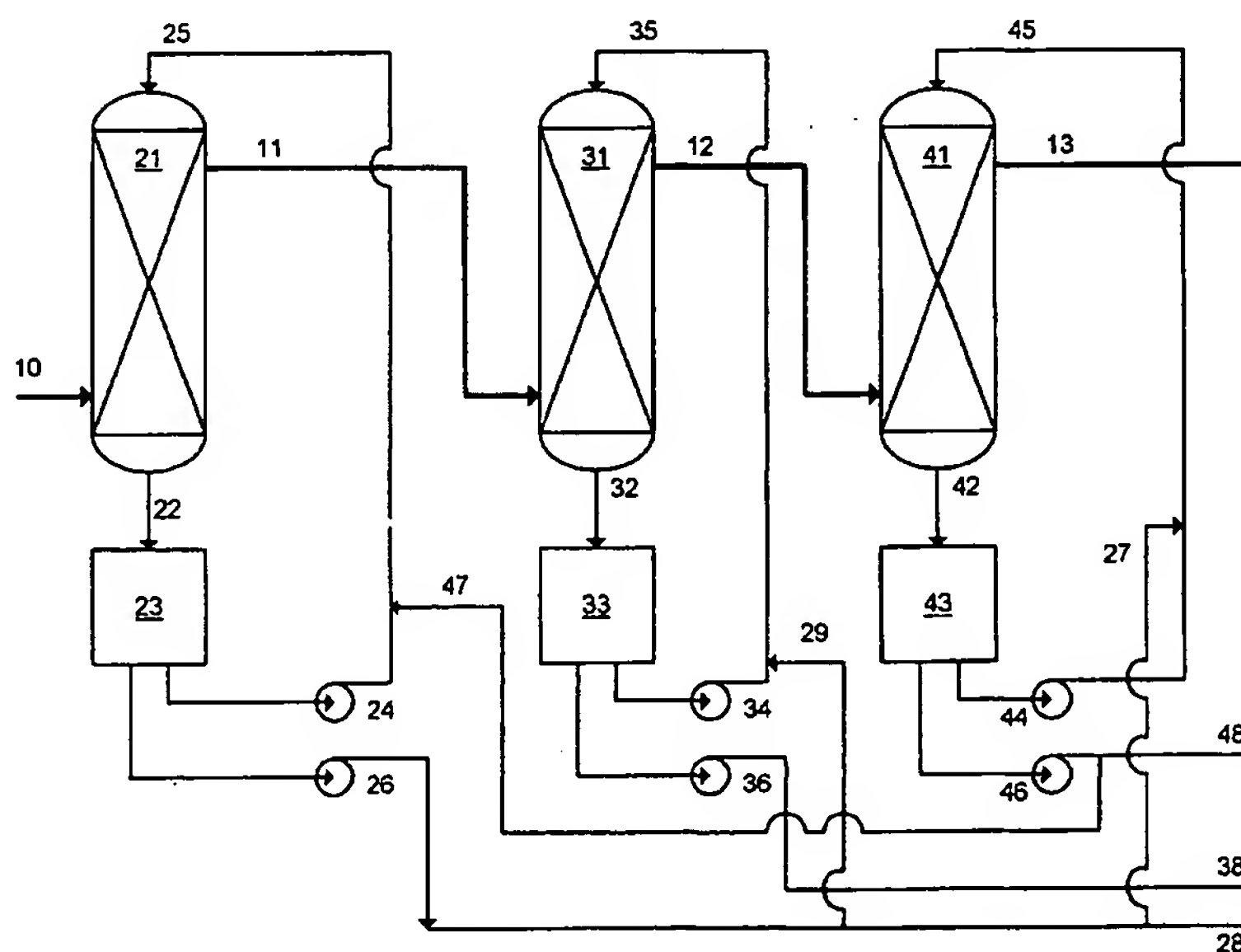
— with international search report

(71) Applicants and

(72) Inventors: **ALIX, Francis** [US/US]; 2310 Ocean Boule-  
vard, Rye, NH 03870 (US). **MCLARNON, Christopher**  
[US/US]; 12 Cottage Street, Exeter, NH 03833 (US).

For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR SCRUBBING FLUE GAS USING ACIDS



(57) Abstract: A process that reduces both NO<sub>x</sub> and SO<sub>2</sub> emissions from the combustion of fossil fuels, comprising at least two steps, is provided. First, the flue gas is contacted with nitric acid (21) to remove SO<sub>2</sub>. Then the flue gas is contacted with sulfuric acid (41) to remove NO<sub>x</sub>. Optionally, a second sulfuric acid contacting step (31) may be used to remove water from the flue gas before the sulfuric NO<sub>x</sub> removing sulfuric acid contacting step (41) so that the temperatures and concentrations of each step may be optimized.

BEST AVAILABLE COPY

PROCESS FOR SCRUBBING FLUE GAS USING ACIDS

by

Francis R. Alix, Christopher R. McLarnon, and Claire A. Golden

5 BACKGROUND

## a. Field of the Invention.

This invention relates to pollution control equipment used for reducing emissions of nitrogen oxides and sulfur dioxide from the burning of fossil fuels.

## b. Description of the Related Art.

10 Nitrogen oxides ("NOx") and sulfur dioxide ("SO<sub>2</sub>") emissions are pollutants commonly emitted from the burning of fossil fuel. NOx (which is understood herein to be predominantly NO and NO<sub>2</sub>) in the atmosphere creates ground level ozone, which is toxic when inhaled. Both SO<sub>2</sub> and NOx contribute to the formation of acid rain, which is harmful to plant and animal life, as well as property.

15 The typical method of reducing NOx emissions is the use of low NOx burners that cool the combustion temperature to a point where the bonds of nitrogen ("N<sub>2</sub>") present in combustion air are less likely to be broken. Breaking the N<sub>2</sub> bond during combustion is what forms NOx in the emissions. Using low NOx burners has the disadvantage of making combustion less efficient and increases particulate matter emissions. Another method of  
20 reducing NOx emissions is to install expensive selective catalytic or non-catalytic reduction systems that use ammonia or urea injection. These devices are expensive to purchase and operate, are prone to fouling, degrade in performance over time, and take up scarce space at plant sites.

The typical methods of reducing SO<sub>2</sub> emissions are burning low-sulfur coal and  
25 employing flue gas desulfurization ("FGD") equipment. Burning low-sulfur coal reduces the particulate matter collecting efficiency of electrostatic precipitators that are commonly used to remove particulate matter emissions. Both of these methods are expensive to build and operate.

One of the features of these methods that make them so expensive to install and  
30 operate is that plants purchase and install a separate control device for each pollutant. Installing a separate device for each pollutant wastes space and money, if a method can be devised that treats more than one pollutant. Also, using one process per pollutant makes it very unlikely that pollutant removal devices can operate synergistically or in a complimentary manner.

For the foregoing reasons, there is a need for a cost-effective process that reduces both NO<sub>x</sub> and SO<sub>2</sub> emissions from the combustion of fossil fuel in a single synergistic process in which the byproducts of the removal of one pollutant aid in the removal of the other pollutant.

5

### SUMMARY

The present invention is directed to a process that satisfies these needs. A cost-effective process that reduces both NO<sub>x</sub> and SO<sub>2</sub> emissions from the combustion of fossil fuel is a two or three step process comprising at least the steps of first oxidizing and  
10 absorbing the SO<sub>2</sub> with nitric acid ("HNO<sub>3</sub>") to form sulfuric acid ("H<sub>2</sub>SO<sub>4</sub>") and additional NO<sub>x</sub> and, second, absorbing the NO<sub>x</sub> with liquid sulfuric acid to form liquid nitrosylsulfuric acid and gas substantially free of NO<sub>x</sub> and SO<sub>2</sub>. The NO<sub>x</sub> produced in the first step is controlled to result in a molar ratio of NO to NO<sub>2</sub> that increases the efficiency of NO<sub>x</sub> removal in the second step. The sulfuric acid produced in the first step also enhances the  
15 ability of the second step to remove NO<sub>x</sub>. These and other features, aspects, and advantages of the present invention will become better understood with reference to the following drawing and description.

### DRAWINGS

20 Fig. 1 is a process schematic that describes the two-step process.

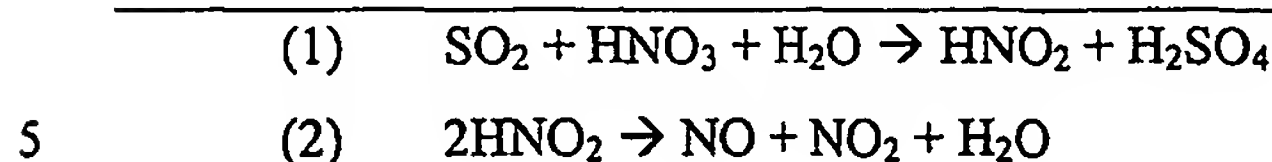
Fig. 2 is a process schematic that describes a three-step process.

### DESCRIPTION

Figure 1 shows the two-step process for removing NO<sub>x</sub> and SO<sub>2</sub>. It is comprised of a  
25 first step where SO<sub>2</sub> is absorbed and oxidized using nitric acid and a second step where NO<sub>x</sub> is absorbed using sulfuric acid. Flue gas 10, containing NO<sub>x</sub> and SO<sub>2</sub> is contacted 21 with liquid nitric acid 25. This contact produces a liquid stream 22 containing a mixture of nitric and sulfuric acids and a gas stream 11 substantially reduced in SO<sub>2</sub>. While gas stream 11 is greatly reduced in SO<sub>2</sub>, the quantity of NO<sub>x</sub> has been greatly increased, which is ordinarily  
30 an undesirable effect, and why oxidizing and absorbing SO<sub>2</sub> with nitric acid has not been used before as a pollution control process. This step also produces sulfuric acid, which is not often desired. Although the first step has not been used for pollution control before, the likely chemical reactions that take place are described in U.S. Patent No. 5,788,949, issued to O'Brien on August 4, 1998, that is not admitted to be prior art by its inclusion herein.

O'Brien teaches a process for converting a source of SO<sub>2</sub> to concentrated H<sub>2</sub>SO<sub>4</sub> in the field of sulfuric acid manufacture. He uses hydrogen sulfide as a source instead of flue gas.

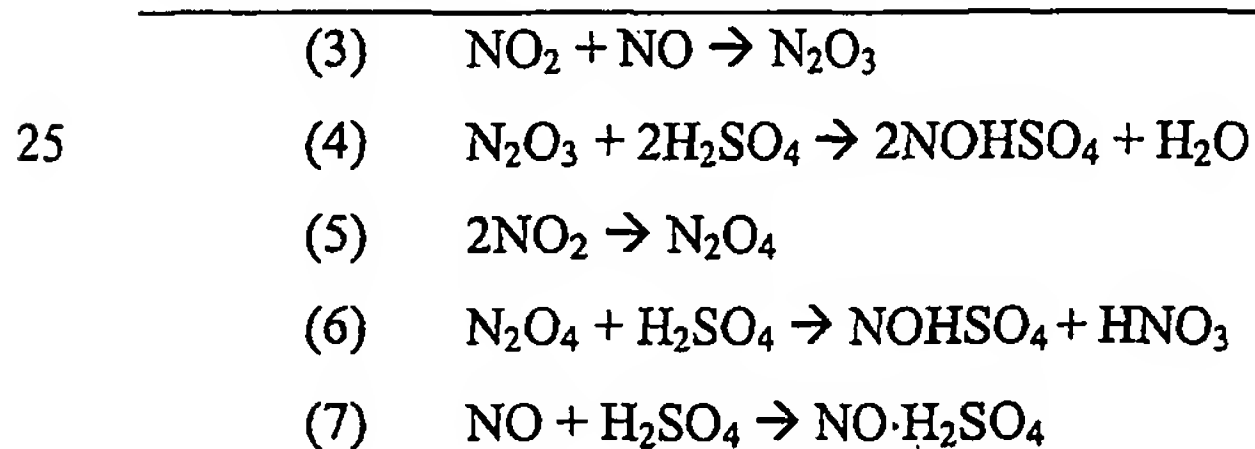
The likely reactions that take place in the first step are as follows:



As taught by O'Brien, these reactions can take place in the liquid phase at temperatures ranging from about 20° C to about 150° C with concentrations of nitric acid from about 0.1 M to about 16 M. Whereas O'Brien teaches that each mole of SO<sub>2</sub> is converted to a half mole of NO and a half mole of NO<sub>2</sub>, we submit only that controlled molar proportions of some sort are important for the second step.

Returning to Figure 1, liquid 22 produced by absorbing and oxidizing SO<sub>2</sub> with nitric acid is a mixture of sulfuric and nitric acids. The liquid mixture 22 enters a separator 23 where the nitric acid and sulfuric acids are separated. This separation may proceed by flash evaporation, evaporation, or other means common to the chemical processing industries. Nitric acid 25 is pumped 24 back to the contactor 21 for reuse in the absorption and oxidation of SO<sub>2</sub>. Sulfuric acid produced in the separator 23 is pumped 26 to the second step of the two-step process 27 or withdrawn as product sulfuric acid 28.

Flue gas 11 from the first process step, containing NO<sub>x</sub> in the form of NO and NO<sub>2</sub>, is brought into contact 41 with sulfuric acid 45. Reactions taking place in the second process step are described in the paper *Absorption of NO<sub>x</sub> Fumes in Sulfuric Acid*, by A. Kaldas, C-I-L Inc., September 1985, which is not admitted to be prior art by its inclusion herein. The major reactions in the second step are as follows:



By these reactions, the NO<sub>x</sub> is converted in the sulfuric acid scrubbing step to liquid nitrosylsulfuric acid ("NOHSO<sub>4</sub>") and violet acid ("NO·H<sub>2</sub>SO<sub>4</sub>"). Violet acid is unstable, and decomposes into nitrosylsulfuric acid. The liquid stream 42, containing sulfuric acid and nitrosylsulfuric acid, is drained from contactor 41. A gas stream 13 is produced which is

substantially free of NO<sub>x</sub> and SO<sub>2</sub>. These reactions occur at a higher rate with higher H<sub>2</sub>SO<sub>4</sub> concentration and lower temperature.

Nitrosylsulfuric acid in the liquid stream 42 produced by the absorption of NO and NO<sub>2</sub> is treated in a processor 43, producing a stream of sulfuric acid 45 substantially free of nitrosylsulfuric acid, pumped by a pump 44 for reuse in the sulfuric acid contactor 41. Removal of nitrosylsulfuric acid in a processor 43 produces nitric acid and is achieved through stream stripping or other methods common to the commercial manufacture of sulfuric acid. Nitric acid produced from nitrosylsulfuric acid is pumped 46 to the first process step 47 to make up for nitric acid consumed in the absorption and oxidation of SO<sub>2</sub>. Nitric acid produced excess of that needed for absorption and oxidation of SO<sub>2</sub> is withdrawn from the process 48.

Product sulfuric acid 28 and nitric acid 48 from the two step process may be sold as commercial acid, utilized in the production of fertilizer, neutralized, or used in other ways as is common for sulfuric and nitric acids.

In practice, the nitric acid scrubbing step 21 could be performed by merely spraying nitric acid into the flue gas stream. Other specific methods include using a packed scrubbing tower, a series of towers, or other mass transfer devices such those that are well known in the pollution control art.

The sulfuric acid scrubbing step 41 may be performed using a packed scrubbing tower, or a series of packed towers or other mass transfer devices that are well known in the pollution control art.

The present invention is suitable for removing NO<sub>x</sub> and SO<sub>2</sub> from the combustion of many types of fossil fuels. The invention may have its broadest application in coal burning electric power plants. However, it should be recognized that this invention could also be used with the combustion of natural gas, propane, oil, diesel fuel, gasoline, wood, biomass, and any other fossil fuel or industrial process that contains sulfur and emits NO<sub>x</sub> and SO<sub>2</sub>.

The process of this invention requires at least two steps to accomplish in a commercially viable system. O'Brien, in U.S. Patent Application No. 09/190,730, filed on 11/10/1998, teaches that SO<sub>2</sub> and NO<sub>x</sub> oxidation can be accomplished in a single step utilizing a mixture of sulfuric and nitric acids. However, experiments treating flue gas representative of that produced by the combustion of fossil fuels have shown that the single step process produces NO<sub>x</sub> in the treated gas in excess of the amount contained in the incoming gas, due to the slow rate of NO<sub>x</sub> absorption. A second step, where NO<sub>x</sub> absorption



takes place without additional SO<sub>2</sub> absorption, is required to achieve a substantial reduction in the emission of nitrogen oxides.

Laboratory experiments conducted in two series packed columns show the ability of the two-step process to remove both SO<sub>2</sub> and NO<sub>x</sub> from simulated flue gas streams. Each column consisted of a 3.8 cm ID glass tube packed to a height of about 46 cm with glass Raschig rings. Simulated flue gas containing SO<sub>2</sub>, NO, NO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub> was passed through the series columns. Nitric acid was circulated through column 1 and sulfuric acid circulated through column 2. Results in the table below show the acid concentration, temperature and flow rate through each column, the gas temperature, flow rate and concentrations of SO<sub>2</sub>, NO and NO<sub>2</sub> at the column inlet and the concentrations of SO<sub>2</sub>, NO and NO<sub>2</sub> at the column outlet.

	Acid			Inlet Gas					Outlet Gas		
	Conc. (wt%)	T (°C)	Flow (cc/min)	T (°C)	Flow (L/min)	SO <sub>2</sub> (ppm)	NO (ppm)	NO <sub>2</sub> (ppm)	SO <sub>2</sub> (ppm)	NO (ppm)	NO <sub>2</sub> (ppm)
Col 1	23%	33	103	33	4.5	1512	527	44	88	955	1000
Col 2	96%	39	24	39	4.5	88	955	1000	80	126	47

It can be seen in the table that liquid nitric acid in contact with gaseous SO<sub>2</sub> substantially reduces the SO<sub>2</sub> concentration (from 1512 to 88 ppm) while producing copious amounts of NO (from 527 to 955 ppm) and NO<sub>2</sub> (from 44 to 1000 ppm). It can also be seen that liquid sulfuric acid substantially reduces the gaseous concentration of NO (from 955 to 126 ppm) and NO<sub>2</sub> (from 1000 to 47 ppm).

It has been determined that nitric acid at a concentration between about 0.1 and 65 percent by weight at a temperature between about 32 and 138° C is effective to absorb and/or oxidize, and therefore remove, SO<sub>2</sub> in the nitric acid contacting step. Likewise, a mixture of nitric acid of between about 0.1 and 65 percent nitric acid by weight and between about 0.1 and 80 percent sulfuric acid by weight will also be effective in the nitric acid contacting step.

In a separate embodiment, shown in Fig.2, removal of SO<sub>2</sub> and NO<sub>x</sub> is accomplished in three processing steps. The first step consists of SO<sub>2</sub> removal utilizing HNO<sub>3</sub> or a mixture of HNO<sub>3</sub> in H<sub>2</sub>SO<sub>4</sub> as described previously. Flue gas 11 from the first step is contacted with sulfuric acid 35 to absorb water vapor creating a flue gas stream 12 that is substantially free of SO<sub>2</sub> and H<sub>2</sub>O. Water removal is accomplished to increase the rate of NO<sub>x</sub> absorption in the third step by allowing the acid 45 utilized in contactor 41 to be more concentrated and at a lower temperature than in the two step process. The affinity of H<sub>2</sub>SO<sub>4</sub> for water, a

common constituent in flue gas steams making up from about three to about fifteen percent of the total volume, is well known. Diluted sulfuric acid stream 32 is then treated in separator 33 producing a sulfuric acid stream 34 returned for additional water absorption. Water from separator 33 is pumped 36 from the process for general use 38 or disposal, as needed.

- 5 Removing water in a separate processing step allows for optimal choice of acid concentration and temperature to accomplish the water removal and recover it from the dehydrating acid stream. It also limits water absorption in the NO<sub>x</sub> removal step , allowing it to be run at an optimal concentration and temperature for NO<sub>x</sub> absorption. Make up sulfuric acid 29 for the water removal step is supplied by the excess sulfuric acid produced in the absorption and  
10 oxidation of SO<sub>2</sub>.

Although the preferred embodiments of the invention are described herein, it will be understood by those skilled in the art that changes and modifications may be made thereto without departing from the spirit of the invention or the scope of the appended claims.

- Accordingly, this specification is intended to encompass all such changes and modifications  
15 that fall within the scope of the present invention.

CLAIMS

We claim:

1. A process for removing SO<sub>2</sub> and NO<sub>x</sub> from a gas stream comprising the steps of
  - a. contacting the gas with a nitric acid solution to remove SO<sub>2</sub> and produce sulfuric acid  
5 and NO<sub>x</sub>, then
  - b. contacting the gas with a sulfuric acid solution to remove NO<sub>x</sub> and produce nitrosylsulfuric acid.
2. The process of claim 1 wherein the solution contacting the gas to remove SO<sub>2</sub> is nitric  
10 acid at a concentration of between 0.1 and 65 percent by weight and at a temperature of between 32 and 138°C.
3. The process of claim 1 wherein the solution contacting the gas to remove SO<sub>2</sub> is a mixture of nitric acid of between 0.1 and 65 percent by weight and sulfuric acid of between 0.1 and 80 percent by weight.
4. The process of claim 1 wherein the solution contacting the gas to remove NO<sub>x</sub> is  
15 sulfuric acid at a concentration of between 65 and 96 percent by weight operating at a temperature of between 21 and 149 °C.
5. The process of claim 1 further comprising the step of treating the nitrosylsulfuric acid from the removal of NO<sub>x</sub> to produce nitric acid.
6. The process of claim 5 wherein at least some of the nitric acid produced is returned to  
20 the SO<sub>2</sub> removal step.
7. A process for removing SO<sub>2</sub> and NO<sub>x</sub> from a gas stream comprising the steps of:
  - a. contacting the gas with a nitric acid solution to remove SO<sub>2</sub> and produce sulfuric acid and NO<sub>x</sub>, then
  - b. contacting the gas with a sulfuric acid solution to remove water vapor from the gas  
25 stream, then
  - c. contacting the gas with a sulfuric acid solution to remove NO<sub>x</sub> and produce nitrosylsulfuric acid.



8. The process of claim 7 wherein the sulfuric acid solution contacting the gas to remove water vapor is provided at a concentration and temperature suitably adapted to remove the water vapor and permit recovery of the water from the sulfuric acid solution.
9. The process of claim 7 wherein the sulfuric acid solution contacting the gas to remove NO<sub>x</sub> is provided at a concentration and temperature suitably adapted to remove the NO<sub>x</sub> and form nitrosylsulfuric acid.
10. An apparatus for removing SO<sub>2</sub> and NO<sub>x</sub> from a gas stream comprising
- a. at least one nitric acid contacting means for contacting the gas stream with nitric acid and thereby removing SO<sub>2</sub>, said nitric acid contacting means having an inlet for receiving a gas stream containing SO<sub>2</sub> and NO<sub>x</sub> and an outlet, and
  - b. at least one sulfuric acid contacting means for contacting the gas stream with sulfuric acid and thereby removing NO<sub>x</sub>, said sulfuric acid contacting means having an inlet for receiving the gas stream from the outlet of said nitric acid contacting means, and an outlet for exhausting the gas stream with SO<sub>2</sub> and NO<sub>x</sub> removed.
11. The apparatus of claim 10 further comprising a separator means for separating nitric acid from sulfuric acid collected from the nitric acid contacting means.
12. The apparatus of claim 10 further comprising a processor means for producing nitric acid from nitrosylsulfuric acid collected from the sulfuric acid contacting means.
13. The apparatus of claim 10 further comprising at least one sulfuric acid contacting means for contacting the gas stream with sulfuric acid and thereby removing water, said sulfuric acid contacting means having an inlet for receiving the gas stream from the outlet of said nitric acid contacting means, and having an outlet for exhausting the gas stream with SO<sub>2</sub> and water removed to said sulfuric acid contacting means for removing NO<sub>x</sub>.
14. The apparatus of claim 13 further comprising a separator means for separating sulfuric acid from water collected from the sulfuric acid contacting means for removing water.

1/2

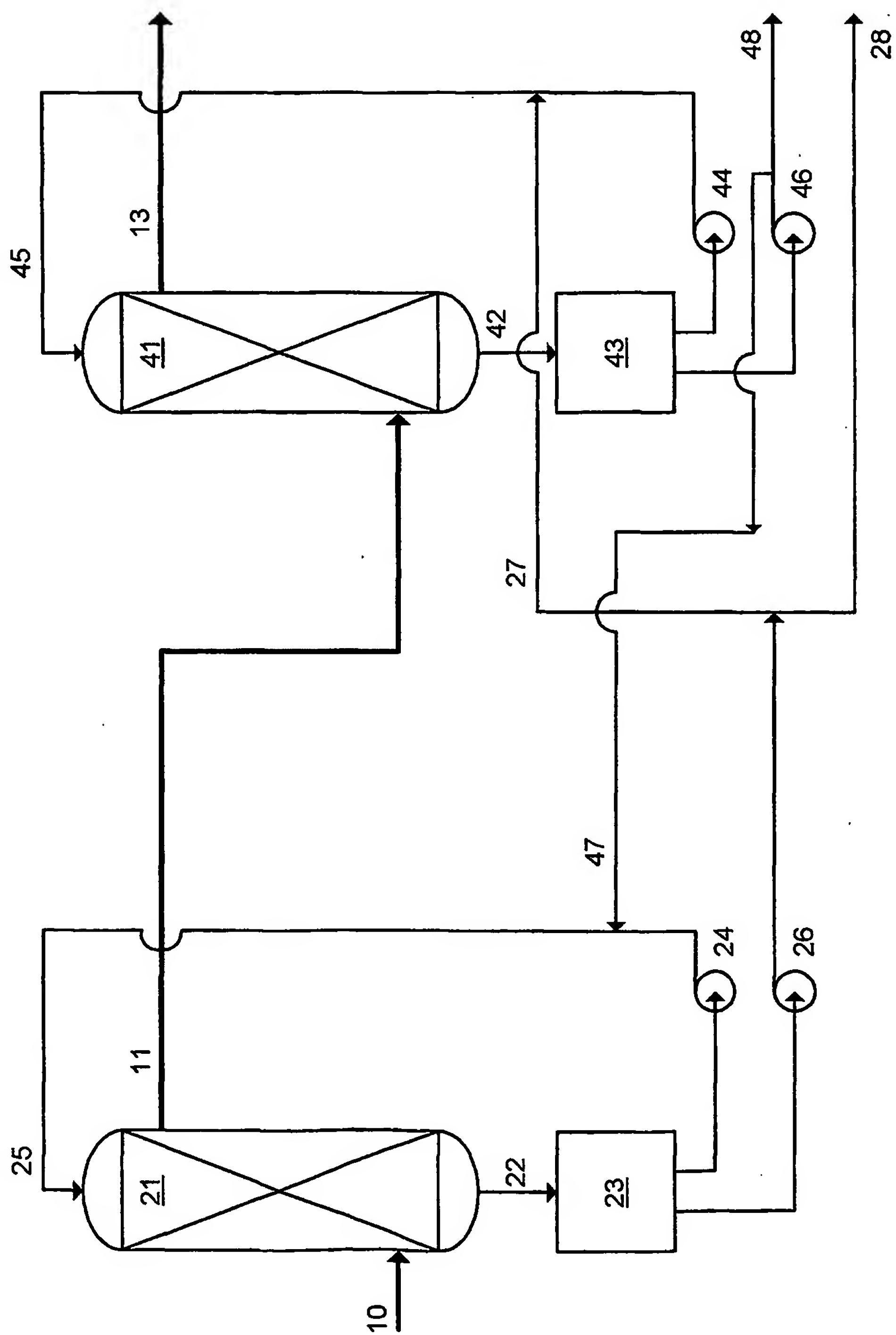


Fig. 1

2/2

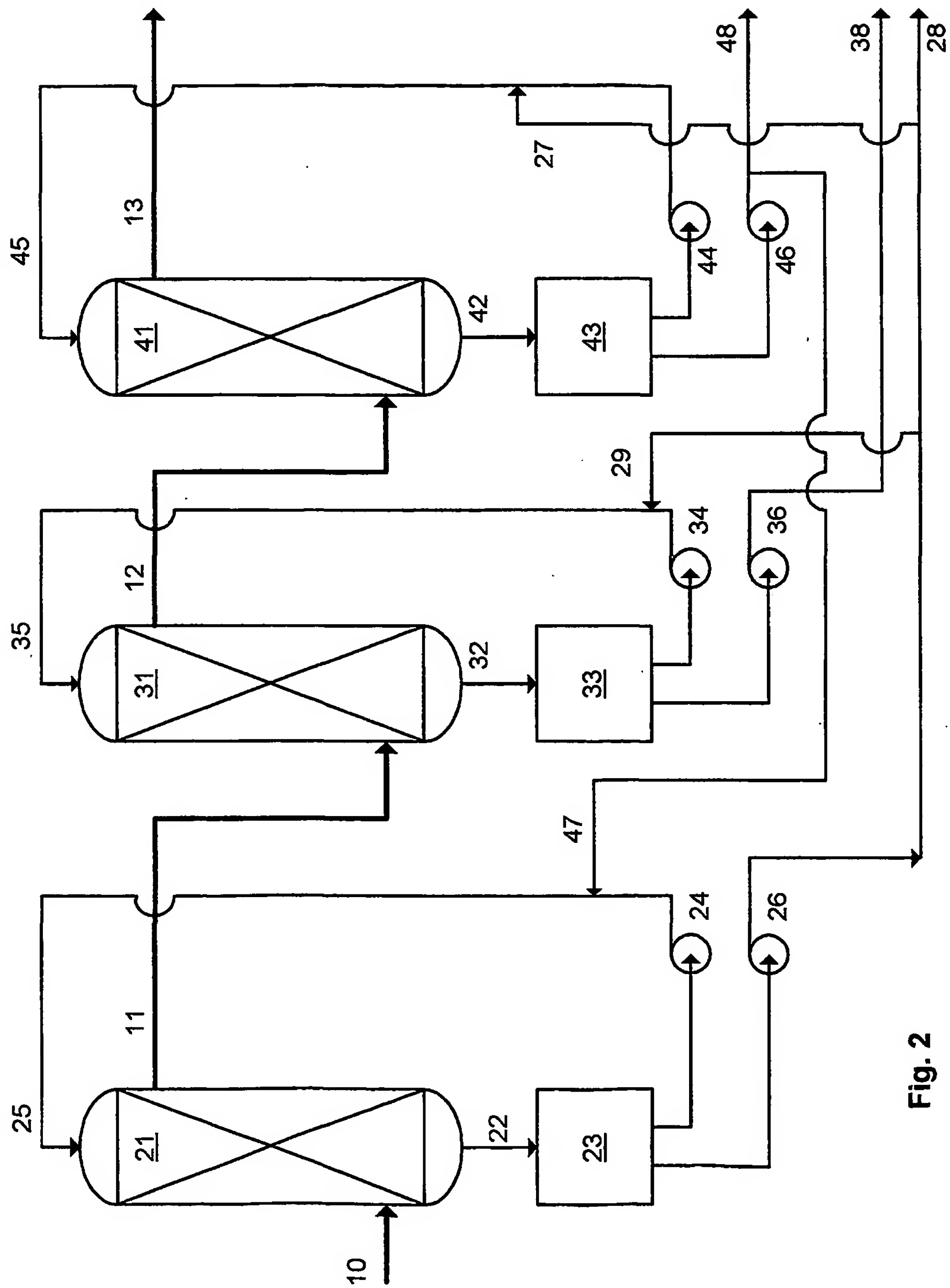


Fig. 2

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US01/15483

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :B01D 53/50; B01J 10/00, 19/00; C01B 17/80, 17/82, 21/38

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 422/160, 161, 168, 169, 170; 423/ 235, 243.01, 388, 390.1, 400, 522, 524

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X — Y	US 4,003,987 A (PAULL et al) 18 January 1977, see col. 1 line 32 to col. 2 line 26.	1, 4, 5, 6, 10 and 12 — 1-14
A	US 2,344,616 A (JENEMANN et al) 21 March 1944, see Fig. 1 and pg. 2, col. 2 line 37 to pg. 3, col. 2 line 38.	1-14
A	US 1,833,418 A (FAIRLIE) 24 November 1931, see Fig. 1 and pg. 1 line 53 to pg. 2 line 87.	1-14

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"A" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

10 JULY 2001

Date of mailing of the international search report

22 AUG 2001

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

TIMOTHY C. VANOY

Telephone No. (703) 308-0661

INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US01/15483

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

422/160, 161, 168, 169, 170; 423/ 235, 243.01, 388, 390.1, 400, 522, 524

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**